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1. Title of the Invention

METHOD FOR MANUFACTURING POLYETHYLENE RESIN EXCELLENT IN MELT FLUIDITY

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[Title of the Document] Specification

1. [Title of the Invention]

METHOD FOR MANUFACTURING POLYETHYLENE RESIN EXCELLENT IN MELT FLUIDITY

2. [Claim]

A method for manufacturing a modified polyethylene resin excellent in melt fluidity and retaining the mechanical strength of the polyethylene, the method comprising graft polymerizing a polymerizable monomer onto a resin by pre-irradiation or simultaneous irradiation with an ionizing radiation, characterized in that the polymerizable monomer is brought into contact with the polyethylene resin in the temperature range of −100°C to −5°C to graft polymerize short graft chains in a low graft ratio.

3. [Detailed Description of the Invention]

The present invention relates to a method for manufacturing a polyethylene resin excellent in melt fluidity. Particularly, the present invention relates to a method characterized in that the melt fluidity of the raw polyethylene is improved while retaining the mechanical strength thereof, by irradiating a polyethylene resin with an ionizing radiation, and thereafter, bringing the polyethylene resin into contact with a polymerizable monomer such as a vinyl monomer at a low temperature in an inert gas atmosphere or under vacuum, or by irradiating a polyethylene resin with an ionizing radiation in the presence of a polymerizable monomer at a low temperature in an inert gas atmosphere or under vacuum to make a graft polymer having a low graft ratio.

Conventional modified polyethylene resins become low in melt fluidity and become quite difficult to mold only by the operation of irradiation with ionizing radiation, or also by the operation of graft polymerization of a vinyl monomer or

the like, losing their versatility and greatly limiting their applications.

Polyethylenes are considered to be the most easily crosslinking resin with ionizing radiation among many resins. Taking advantage of the crosslinking effect, molded products such as films, tubes, sheets and the like made of a polyethylene resin that are irradiated with ionizing radiation and thus given properties including chemical resistance and abrasion resistance are commercially available. The present situation, where only the irradiation of molded products is industrialized, is based mainly on the fact that since radiation irradiation decreases the melt fluidity of polyethylenes and thus reduces the moldability, the molding process after the irradiation of objects having raw material shapes is not possible.

Graft polymerization onto polyethylenes by radiation irradiation are much often attempted as means to impart properties including impact resistance, adhesiveness and dyeability, but the melt fluidity of graft polymers reportedly decreases generally with the graft polymerization operation, and further with increasing graft ratio. There are no precedent in which graft polymerization is utilized to improve the melt fluidity because a decrease in moldability cannot be prevented even after radiation irradiation or graft polymerization.

It is an objective of the present invention to provide a method for manufacturing a modified polyethylene resin excellent in melt fluidity and retaining the mechanical strength of a polyethylene. It is another objective of the present invention to eliminate a conventional drawback of a decrease in the melt fluidity decreasing due to irradiation with ionizing radiation, and to enable radiation irradiation of objects having raw material shapes such as powder by making a graft polymer by irradiating a polyethylene resin with ionizing radiation and bringing the resin into contact with a

polymerizable monomer such as a vinyl monomer in a special temperature range of low temperatures in an atmosphere having no coexisting molecular oxygen and moreover by adjusting its graft ratio to a low one.

The present invention has a technical idea quite different from conventional graft polymerization onto polyethylenes. The conventional graft polymerization onto polyethylenes technically aims exclusively at improvement in the graft ratio and elongation of graft chains. Therefore, the radiation graft method aims to perform graft polymerization at ordinary temperature or at a temperature higher than that to increase the graft ratio as much as possible to modify a polyethylene to a direction different from the present invention. By contrast, the present invention is to provide a grafted polyethylene having a novel property by performing graft polymerization at a low temperature of not more than about −5°C to decrease the graft ratio reasonably and shorten the graft chains reasonably.

Technically examining the unexpected effect of the present invention, one conceivable factor for the effect is that short-chain graft branches produced by a graft polymerization of a low degree at a low temperature improves the melt fluidity and simultaneously, the generation of reasonable crosslinking of a polyethylene by radiation irradiation retains its mechanical strength. Therefore, from this view point, it can be said that the advantage of the present invention lies in a synergistic effect of short-chain graft branches and crosslinked polyethylene.

The representative constitution and mode of the present invention will be described hereinafter. A polyethylene resin is irradiated with an ionizing radiation in an inert gas such as air or nitrogen or under vacuum in the temperature range of −100°C to ordinary temperature, and then brought into contact with a polymerizable monomer singly or a mixed monomer of two or more monomers in a liquid phase or gas phase in an inert

gas such as nitrogen or under vacuum at a predetermined temperature of not more than −5°C for a predetermined time to obtain a graft polymer having a low graft ratio. The purpose of adjusting the graft ratio to a low one lies in making graft chains reasonable ultrashort chains. Single polymers produced as byproduct are washed and removed with an organic solvent such as acetone, benzene or tetrahydrofuran. In the case where a polyethylene resin is irradiated with an ionizing radiation in the presence of a polymerizable monomer, although the polymerization must be performed in an inert gas such as nitrogen or under vacuum, the conditions other than the atmosphere are the same as described above.

Any of low density, middle density, and high density polyethylenes can be used as the raw polyethylene. The shapes are powders, films, sheets or the like, but preferably powders in view of having a broad application range.

Ionizing radiation refers to γ rays, electron beams, X rays, β rays, α rays, proton beams, deuteron beams and the like.

Polymerizable monomer refers to, for example, vinyl chloride, vinyl acetate and ethyl acrylate; and every one of those which are liquid or gaseous at the graft polymerization temperature can be used, and solid ones need to be used as a solution. These monomers may be used singly or as a mixture of two or more; and in the case of using a monomer as a solution, the monomer needs to be dissolved in an organic solvent such as methanol, ethanol, acetone or toluene.

The reaction temperature is in the range of −100°C to about −5°C, and preferably −80°C to −20°C. The irradiation dose is normally about 0.05 Mrad to 6 Mrad, and desirably 1 Mrad to 3 Mrad. A low graft ratio normally refers to a graft percentage in the range of about 0.01 graft% to about 3 graft%, and desirably 0.05 graft% to 1 graft%. The reaction time, depending on the monomer used, is a suitable time in which the graft ratio falls in a low graft ratio, for example, 10 min to

3 hours. In the case of a high grafting rate, for example, in the case where the contact time with a monomer must be elongated, addition of a chain transfer agent such as acetoaldehyde, mercaptan or carbon tetrachloride can adjust graft chains.

Examples will be shown hereinafter to describe the present invention further in detail. These Examples are for exemplifying representative modes of the present invention, and do not limit the scope of the present invention. It is fully understood to those skilled in the art that changes and modifications may be made within the spirit and the scope of the present invention. Ingredient amounts in Examples are based on weights unless otherwise specified. The melt index (g/10 min, 190°C, 2.16 kg) was employed as an index of the melt fluidity of a polyethylene.

Example 1

300 parts of a powdery high-density polyethylene (density, 0.955; melt index, 5.0 [g/10 min]) was irradiated with 3 Mrad of an electron beam in air at a temperature of –78°C by an electron beam accelerator (2 MeV, 1 mA). 100 parts thereof (referred to as a radiation-irradiated polyethylene) was allowed to stand at room temperature, and blended with 0.5 part of 2,6-di-t-butylcresol. The melt index after the blending was 4.0; the tensile strength at 20°C was 201.6 kg/cm^2; the Izod impact strength was 4.5 kg·cm/cm^2. Another 100 parts thereof was mixed with 200 parts of a vinyl chloride monomer under vacuum at a temperature of –50°C for 60 min, quickly filtered, and washed with acetone and dried to thereby obtain a graft polymer having a graft ratio of 0.05%. The graft polymer was blended with 0.5 part of dibutyltin maleate. The melt index was 7.3; the tensile strength at 20°C was 210 kg/cm^2; and the Izod impact strength was 4.1 kg·cm/cm^2. The rest 100 parts thereof was mixed with 200 parts of a mixed monomer of vinyl chloride and vinyl acetate (weight ratio, VC/VAC = 7/3) in a nitrogen gas flow at –50°C for 60 min, and

washed with tetrahydrofuran and dried. The dried product had a graft ratio of 0.36%; and the melt index after being blended with 1 part of dibutyltin maleate improved to 7.8. The blended product exhibited a tensile strength of 203.5 kg/cm^2 and an Izod impact strength of 4.4 kg·cm/cm^2 at a temperature of 20°C.

Example 2

The same powdery high-density polyethylene as in Example 1 was irradiated with 3 Mrad of an electron beam in a nitrogen atmosphere at a temperature of −78°C. The radiation-irradiated polyethylene had a melt index of 3.5. The polyethylene was mixed with a mixed monomer of vinyl chloride (VC) and vinyl acetate (VAC) (weight ratio, VC/VAC = 7/3) at a temperature of −70°C under vacuum for 60 min to obtain a graft polymer having a graft ratio of 0.02%; and the graft polymer had a melt index of 6.8; and the graft polymer obtained by mixing for 180 min had a graft ratio of 1% and a melt index of 6.4. Further in the case of mixing with ethyl acrylate at a temperature of −30°C under vacuum for 10 min, the graft polymer had a graft ratio of 0.02% and a melt index of 6.4.

Example 3

The irradiated polyethylene obtained by irradiating the same powdery high-density polyethylene as in Example 1 with 1 Mrad of an electron beam had a melt index of 4.5. The irradiated polyethylene was immersed and stirred in a toluene solution of methylene in a nitrogen gas flow at a temperature of −20°C for 30 min to obtain a graft polymer having a graft ratio of 0.01% and a melt index of 5.5. In the case where a small amount of carbon tetrachloride was added to the system of the same composition, and mixed for 50 min, a graft polymer having a graft ratio of 0.01% and a melt index of 5.6 was obtained.

Example 4

A powdery high-density polyethylene (density, 0.960; melt index, 8.0) was irradiated with 3 Mrad of an electron beam in

air at a temperature of −78°C. The obtained irradiated polyethylene had a melt index of 0.75. The irradiated polyethylene was mixed with a vinyl chloride monomer at −50°C under vacuum for 10 min to obtain a graft polymer having a graft ratio of 0.06% and a melt index of 1.4. A graft polymer obtained by mixing for 30 min had a graft ratio of 0.1% and a melt index of 1.3. No difference was observed in the tensile strength and impact strength at 20°C between the irradiated polyethylene and the graft polymers.

<u>Example 5</u>

A powdery high-density polyethylene (density, 0.919; melt index, 1.2) was mixed with vinyl chloride whose amount was enough for the powder to be immersed under vacuum, and irradiated with 1 Mrad of γ rays from a Co-60 radiation source (for 1 hour at 10^6 R/hr) at −70°C. The polyethylene irradiated with 1 Mrad of γ rays had a melt index of 0.24, whereas the graft polymer having a graft ratio of 0.05% had a melt index of 0.63. Comparing the irradiated polyethylene and the graft polymer, no difference was observed in the tensile strength and impact strength between them.

Improvements in heat resistance, chemical resistance, abrasion resistance and the like can be aimed at by irradiating final moldings such as films, tubes and sheets made of polyethylene resins with an ionizing radiation, but if powders, films or the like, which are conventional molding raw materials, are irradiated with a radiation, the melt fluidity thereof decreases, so molding these is remarkably difficult. According to the present invention, the combination of radiation irradiation and low-temperature low-grafting polymerization provides a polyethylene having mechanical strength equal to that of radiation-irradiated polyethylenes and having a higher melt fluidity than the radiation-irradiated polyethylenes. Accordingly, the present invention has an advantage that allows objects having raw material

shapes of powder and the like to be irradiated with a radiation.

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5. List of Attached Documents

(1) Power of Attorney 1 copy (to be supplemented later)

(2) Certificate defined by the provision of Patent Law Section 30(4) 1 copy (to be supplemented later)

(3) Specification 1 copy